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14. ABSTRACT
A number of JANNAF publications have illustrated the remarkable performance modification that the addition of Tag-ZT can have in formulations of energetic materials, where the Tag-ZT additive resulted in significant improvement in performance the energetic material. Recent studies in the research lab or Dr Rich Behrens have demonstrated that the thermal reaction of TAG-ZT results in formation of hydrazine, N2H4. The Behrens' group further evaluate the hydrazine to be a primary contributor to the beneficial results of the TAG ZT additive. This study identifies a number of common N2H3 containing hydrocarbons, determines their thermochemistry and kinetic parameters for dissociation to a hydrocarbon and hydrazine

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Report Title

Thermochemistry and Kinetics for Designer Molecules, Additives to Energetic Materials for Improved Performance:I Thermal Generation of Hydrazine by some common nitrogen hydrocarbons.

ABSTRACT

A number of JANNAF publications have illustrated the remarkable performance modification that the addition of Tag-ZT can have in formulations of energetic materials, where the Tag-ZT additive resulted in significant improvement in performance the energetic material. Recent studies in the research lab or Dr Rich Behrens have demonstrated that the thermal reaction of TAG-ZT results in formation of hydrazine, N2H4. The Behrens' group further evaluate the hydrazine to be a primary contributor to the beneficial results of the TAG ZT additive. This study identifies a number of common N2H3 containing hydrocarbons, determines their thermochemistry and kinetic parameters for dissociation to a hydrocarbon and hydrazine using computational chemistry. Experimental studies are suggested for verification of the results and for modelers to identify desired molecular formulations for the NJIT group to target structures that match the needed properties.

Technology Transfer ARO Contract W911NF0710106

– Design Molecules identified by use of Computational Chemistry for Formation of hydrazine, which is identified by Behren experiments to be key component in TAG-zT decomposition leading to improved energetic performance.

Thermochemistry and Kinetics for Designer Molecules
Additives to Energetic Materials for Improved Performance

Thermal Generation of Hydrazine

New Jersey Institute of Technology, Newark, NJ 07102

A number of JANNAF publications have illustrated the remarkable performance modification that the addition of TAG-ZT can have in formulations of energetic materials. Here the Tag-ZT additive resulted in significant improvement in performance the energetic material. Recent studies in the research lab or Dr Rich Behrens have demonstrated that the thermal reaction of TAG-ZT results in formation of hydrazine, N_2H_4. The Behrens' group further evaluate the hydrazine to be a primary contributor to the beneficial results of the TAG ZT additive. Additional studies by the Research Group of Stefan Tynell at Penn State also illustrate the formation of hydrazine (N2H4) from TAG-ZT.

We have selected twelve initial, stable, molecule structures and evaluated the thermochemistry and kinetics of a four center (retro-ene) elimination reaction to generate (form) hydrazine via thermal treatment. We have used computational chemistry to determine the thermochemical and kinetic parameters for the reactions of these molecules and identify two molecules that are commercially available for possible experimental testing. We show reaction barriers that range between 36 and 65 kcal mol-1; this barrier range provides a wide temperature window for insertion of the N_2H_4 into the energetic material reaction process from thermal decomposition of the additive. Several additive molecules contain limited hydrocarbon component, to limit undesired chemistry interaction.

We look to further collaborations of the research group and advisors that Dr William Anderson has assembled to identify the desired and non desired components of the hydrazine sources in order to design more precursors for application to energetic materials. We also look forward to possible experimental testing to verify and calibrate our computation results.

The thermochemical and kinetic parameters are developed using computational chemistry at the B3LYP Density Functional, Moller Plesset ab initio, and the CBS-QB3 (Complete Basis Set) computational chemistry methods. In each case the elimination of hydrazine from the parent compound involves a hydrogen shift via a four-membered ring transition state in a concerted reaction which also forms a pi (sp^2 double) bond, from a stable, synthetically feasible, parent compound. The parent compounds fall into two general motifs: (i.) linear (straight chain) moieties that undergo hydrogen shifts between secondary nitrogen or carbon atoms and (ii.) branched (isopropyl- or tert-butyl groups) on the atom from which the the hydrazinic (N_2H_3--) group is bonded. The branched precursors could be of immediate use in experiments, as a proof of concept, as both isopropyl- and tert-butyl substituted hydrazine are commercially available. In addition we are confident we can identify molecules with more nitrogen or other elements such as silicon, or sulfur, phosphorous, in place of hydrocarbon structures in the current set.

The activation energy required for these reactions was relatively independent of the connecting group to the hydrazine moiety, but the reaction enthalpies are strongly related to both the thermochemistry of the reaction and the bond dissociation energy of the hydrogen atom, which is being moved to the N_2H_3 group. Activation energies for the elimination reactions are near 44 kcal mol^{-1} in the molecules where the R—H bond is weak (on a scale relative to a alkyl- C--H bond) and near 61 kcal mol^{-1} when hydrogen is removed from a typical alkyl carbon (C—H) are determined.

Rate constants are being further optimized by additional analysis on the contributions to S(T) and Cp(T) from internal rotors in place of the calculation estimates using computational chemistry generated torsion frequency estimates. Details of the thermochemistry including our initial internal rotor analysis are in the appendix, along with the thermochemical data and the pre-exponential (A-factors) for the reactions. Enthalpy barriers for a number of represented precursor compounds for hydrazine formation reaction are listed in Table I.

The calculations reveal several compounds, which may act as viable hydrazine precursors in thermal systems and possible optimization approach for its injection into energetic applications. The range of activation barriers provides a range of temperatures and lifetimes of the hydrazine precursor(s) and the trends provide suggestions for design of molecules with lower or higher barriers and design or optimization of hydrazine injection to the process.

We also look to information from the Army and Navy researchers as to which elements are preferred to be in the source compounds, elements that will either contribute beneficially to the energetic process or that will not have a negative effect.

Enthalpy and other thermochemical and reaction kinetic parameters will be improved by incorporating the CBS-QB3 calculation energies and by improving the the entropy $S^{o}(T)$ and heat capacity Cp(T) contributions from values further analysis of the internal rotors. Preliminary data suggests that the errors from the above assumptions are offsetting and the kinetics will remain similar.

Improvements, higher level calculations, are partially complete and in progress.

Table I

Representative listing of N_2H_3 Precursor Compounds and Reaction Barriers

Compound	Method	Activation Enthalpy $\Delta_f H^{\ddagger}_{(298)}$	Reaction Enthalpy ΔH_{rxn}
$CH2(N_2H_3)_2$	B3LYP/6-311G(d,p)	**43.01**	**-0.7**
$CH2(N_2H_3)(CH_2NH_2)$	B3LYP/6-311G(d,p)	**58.3**	**5.8**
$O(N_2H_3)(CH_2NH_2)$	B3LYP/6-311G(d,p)	**61.7**	**-42.0**
$S(N_2H_3)_2$	MP2/6-311++G(2df,p)	**41.8**	**5.1**
$S(N_2H_3)(CH_2NH_2)$	MP2/6-311G(d,p)	**41.95**	**-9.9**
$NH=C(N_2H_3)_2$	B3LYP/6-311G(d,p)	**38.5**	**25.8**
$NH=C(N_2H_3)(CH_2NH_2)$	B3LYP/6-311G(d,p)	**66.1**	**32.3**
$O=C(N_2H_3)_2$	B3LYP/6-311G(d,p)	**45.4**	**31.8**
$CH(N_2H_3)(CH_3)_2$	B3LYP/6-311G(d,p)	**65.8**	**19.0**
$C(N_2H_3)(CH_3)_3$	B3LYP/6-311G(d,p)	**65.5**	**17.2**
$N(N_2H_3)(CH_3)_2$	MP2/6-311G(d,p)	**66.8**	**-4.8**
$C(N_2H_3)(NH_2)_2$	B3LYP/6-311G(d,p)	**50.7**	**10.3**

The central atom, which is the atom adjacent to the N_2H_3 group is listed along with its other substituents. Enthalpies are in (kcal mol^{-1}).

THERMODYNAMIC and KINETIC ANALYSIS for the above REACTIONS

Thermochemical units are calories mol^{-1} or kcal mol^{-1}

Rate constants are unimolecular dissociations and in units of sec^{-1}

THERMODYNAMIC ANALYSIS for REACTION

Rx	C(N2H3)2	= T_C(N2H3)2
Hf {Kcal/mol}	68.540	111.550
S {cal/mol K}	99.300	77.130

Fit Af/Ar : A = 1.362E-07 n = .86 alpha = 1.721E-03 avg error 17.39 %
Fit Af/Ar w/ddU: A = 1.215E-09 n = 1.73 alpha = 3.171E-03 avg error 35.28 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	4.301E+01	4.301E+01	-2.218E+01	6.592E-37	4.966E+01
400.00	4.285E+01	4.285E+01	-2.264E+01	4.345E-29	5.191E+01
500.00	4.277E+01	4.277E+01	-2.282E+01	2.071E-24	5.418E+01
600.00	4.275E+01	4.275E+01	-2.286E+01	2.699E-21	5.646E+01
800.00	4.278E+01	4.278E+01	-2.282E+01	2.114E-17	6.103E+01
1000.00	4.278E+01	4.278E+01	-2.281E+01	4.603E-15	6.559E+01
1200.00	4.261E+01	4.261E+01	-2.297E+01	1.657E-13	7.017E+01
1500.00	4.176E+01	4.176E+01	-2.358E+01	5.751E-12	7.714E+01
2000.00	3.819E+01	3.819E+01	-2.560E+01	1.701E-10	8.939E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 4.6634E+06 n = .58701 Ea = 4.3258E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	8.863E+07	2.845E+01	4.120E-24	4.046E-24
400.00	9.398E+07	3.368E+01	3.621E-16	3.625E-16
500.00	1.073E+08	3.840E+01	2.158E-11	2.206E-11
600.00	1.258E+08	4.274E+01	3.374E-08	3.480E-08
800.00	1.715E+08	5.060E+01	3.523E-04	3.584E-04
1000.00	2.151E+08	5.768E+01	9.591E-02	9.440E-02
1200.00	2.389E+08	6.419E+01	4.143E+00	3.956E+00
1500.00	2.188E+08	7.318E+01	1.797E+02	1.698E+02
2000.00	1.057E+08	8.664E+01	7.088E+03	7.569E+03

THERMODYNAMIC ANALYSIS for REACTION

Rx **C(N2H3)(CNH4) = T_C(N2H3)(CNH4)**
Hf {Kcal/mol} 38.760 97.040
S {cal/mol K} 97.900 78.700

Fit Af/Ar : A = 6.966E+00 n = -2.18 alpha =-3.086E-03 avg error 6.46 %
Fit Af/Ar w/ddU: A = 2.641E+04 n = -3.75 alpha =-5.549E-03 avg error 8.81 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	5.828E+01	5.828E+01	-1.921E+01	2.203E-47	6.404E+01
400.00	5.814E+01	5.814E+01	-1.959E+01	8.842E-37	6.598E+01
500.00	5.802E+01	5.802E+01	-1.986E+01	1.970E-30	6.795E+01
600.00	5.793E+01	5.793E+01	-2.003E+01	3.300E-26	6.995E+01
800.00	5.785E+01	5.785E+01	-2.015E+01	6.160E-21	7.397E+01
1000.00	5.798E+01	5.798E+01	-2.002E+01	8.970E-18	7.800E+01
1200.00	5.837E+01	5.837E+01	-1.966E+01	1.177E-15	8.197E+01
1500.00	5.957E+01	5.957E+01	-1.878E+01	1.640E-13	8.774E+01
2000.00	6.330E+01	6.330E+01	-1.667E+01	2.753E-11	9.663E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 7.7060E+04 n = 1.34134 Ea = 5.7705E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.959E+08	2.102E+03	1.377E-34	1.472E-34
400.00	4.348E+08	3.092E+03	7.369E-24	7.012E-24
500.00	4.752E+08	4.171E+03	2.053E-17	1.915E-17
600.00	5.224E+08	5.326E+03	4.126E-13	3.912E-13
800.00	6.558E+08	7.835E+03	1.027E-07	1.036E-07
1000.00	8.785E+08	1.057E+04	1.869E-04	1.988E-04
1200.00	1.261E+09	1.350E+04	2.942E-02	3.211E-02
1500.00	2.453E+09	1.821E+04	5.127E+00	5.479E+00
2000.00	9.486E+09	2.678E+04	1.147E+03	1.019E+03

THERMODYNAMIC ANALYSIS for REACTION

Rx **O(N2H3)(CNH4) = T_O(N2H3)(CNH4)**
Hf {Kcal/mol} 27.220 88.940
S {cal/mol K} 96.230 79.470

Fit Af/Ar : A = 1.249E+00 n = -1.60 alpha =-1.983E-03 avg error 9.38 %
Fit Af/Ar w/ddU: A = 1.215E+03 n = -2.88 alpha =-3.753E-03 avg error 15.81 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	6.172E+01	6.172E+01	-1.676E+01	2.345E-49	6.675E+01
400.00	6.166E+01	6.166E+01	-1.693E+01	4.048E-38	6.843E+01
500.00	6.157E+01	6.157E+01	-1.712E+01	2.195E-31	7.014E+01
600.00	6.147E+01	6.147E+01	-1.730E+01	6.669E-27	7.186E+01
800.00	6.129E+01	6.129E+01	-1.757E+01	2.598E-21	7.535E+01
1000.00	6.121E+01	6.121E+01	-1.766E+01	5.770E-18	7.887E+01
1200.00	6.132E+01	6.132E+01	-1.757E+01	9.820E-16	8.240E+01
1500.00	6.196E+01	6.196E+01	-1.710E+01	1.717E-13	8.761E+01
2000.00	6.460E+01	6.460E+01	-1.560E+01	3.383E-11	9.581E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 4.3707E+06 n = .97096 Ea = 6.1579E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	1.356E+09	2.542E+02	1.466E-36	1.518E-36
400.00	1.660E+09	3.361E+02	3.374E-25	3.302E-25
500.00	1.884E+09	4.174E+02	2.287E-18	2.201E-18
600.00	2.066E+09	4.983E+02	8.338E-14	8.051E-14
800.00	2.413E+09	6.589E+02	4.331E-08	4.317E-08
1000.00	2.877E+09	8.182E+02	1.202E-04	1.242E-04
1200.00	3.617E+09	9.767E+02	2.455E-02	2.596E-02
1500.00	5.727E+09	1.213E+03	5.365E+00	5.643E+00
2000.00	1.619E+10	1.604E+03	1.410E+03	1.306E+03

THERMODYNAMIC ANALYSIS for REACTION

Rx **O*C(N2H3)2 = T_O*C(N2H3)**2
Hf {Kcal/mol} 5.550 50.950
S {cal/mol K} 97.550 82.330

Fit Af/Ar : A = 5.566E-04 n = -.07 alpha =-9.504E-04 avg error 3.71 %
Fit Af/Ar w/ddU: A = 5.788E-04 n = -.09 alpha =-1.461E-03 avg error 7.49 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	4.540E+01	4.540E+01	-1.521E+01	3.952E-37	4.997E+01
400.00	4.551E+01	4.551E+01	-1.491E+01	7.500E-29	5.147E+01
500.00	4.560E+01	4.560E+01	-1.471E+01	7.126E-24	5.295E+01
600.00	4.569E+01	4.569E+01	-1.454E+01	1.507E-20	5.441E+01
800.00	4.588E+01	4.588E+01	-1.426E+01	2.222E-16	5.729E+01
1000.00	4.613E+01	4.613E+01	-1.399E+01	7.240E-14	6.012E+01
1200.00	4.647E+01	4.647E+01	-1.368E+01	3.513E-12	6.289E+01
1500.00	4.721E+01	4.721E+01	-1.313E+01	1.779E-10	6.691E+01
2000.00	4.909E+01	4.909E+01	-1.206E+01	9.965E-09	7.322E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 8.5048E+04 n = 1.69040 Ea = 4.4906E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	2.957E+09	1.539E+04	2.470E-24	2.515E-24
400.00	4.582E+09	2.503E+04	6.251E-16	6.179E-16
500.00	6.364E+09	3.650E+04	7.424E-11	7.281E-11
600.00	8.293E+09	4.968E+04	1.884E-07	1.852E-07
800.00	1.271E+10	8.079E+04	3.704E-03	3.702E-03
1000.00	1.825E+10	1.178E+05	1.509E+00	1.534E+00
1200.00	2.559E+10	1.603E+05	8.784E+01	9.028E+01
1500.00	4.212E+10	2.338E+05	5.561E+03	5.692E+03
2000.00	9.615E+10	3.802E+05	4.153E+05	4.002E+05

THERMODYNAMIC ANALYSIS for REACTION

Rx **HN*C(N2H3)2 = T_HN*C(N2H3)2**
Hf {Kcal/mol} 69.690 108.180
S {cal/mol K} 95.480 82.080

Fit Af/Ar : A = 1.026E-06 n = 1.39 alpha = 2.297E-03 avg error 12.47 %
Fit Af/Ar w/ddU: A = 6.352E-08 n = 1.99 alpha = 3.702E-03 avg error 29.08 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	3.850E+01	3.850E+01	-1.338E+01	1.069E-31	4.251E+01
400.00	3.876E+01	3.876E+01	-1.261E+01	1.159E-24	4.380E+01
500.00	3.890E+01	3.890E+01	-1.229E+01	2.033E-20	4.505E+01
600.00	3.893E+01	3.893E+01	-1.223E+01	1.393E-17	4.627E+01
800.00	3.873E+01	3.873E+01	-1.251E+01	4.831E-14	4.874E+01
1000.00	3.826E+01	3.826E+01	-1.303E+01	6.161E-12	5.129E+01
1200.00	3.762E+01	3.762E+01	-1.361E+01	1.489E-10	5.395E+01
1500.00	3.654E+01	3.654E+01	-1.441E+01	3.353E-09	5.816E+01
2000.00	3.506E+01	3.506E+01	-1.527E+01	6.759E-08	6.561E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 4.8394E+09 n = .33707 Ea = 3.9430E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	7.440E+09	6.839E+00	6.682E-19	6.201E-19
400.00	1.458E+10	7.535E+00	9.662E-12	1.039E-11
500.00	2.142E+10	8.124E+00	2.118E-07	2.281E-07
600.00	2.655E+10	8.638E+00	1.742E-04	1.810E-04
800.00	3.080E+10	9.518E+00	8.052E-01	7.773E-01
1000.00	2.963E+10	1.026E+01	1.284E+02	1.196E+02
1200.00	2.653E+10	1.091E+01	3.723E+03	3.474E+03
1500.00	2.215E+10	1.176E+01	1.048E+05	1.023E+05
2000.00	1.912E+10	1.296E+01	2.817E+06	3.079E+06

THERMODYNAMIC ANALYSIS for REACTION

Rx **HN*C(N2H3)(CNH4) = T_HN*C(N2H3)(CNH4)**

Hf {Kcal/mol} 47.810 119.450

S {cal/mol K} 97.900 83.160

Fit Af/Ar : A = 5.660E+03 n = -2.89 alpha =-2.951E-03 avg error 39.27 %

Fit Af/Ar w/ddU: A = 2.305E+10 n = -5.66 alpha =-6.204E-03 avg error 83.22 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	7.164E+01	7.164E+01	-1.473E+01	3.840E-56	7.606E+01
400.00	7.168E+01	7.168E+01	-1.460E+01	4.360E-43	7.752E+01
500.00	7.157E+01	7.157E+01	-1.485E+01	2.944E-35	7.899E+01
600.00	7.134E+01	7.134E+01	-1.527E+01	4.741E-30	8.050E+01
800.00	7.070E+01	7.070E+01	-1.618E+01	1.405E-23	8.364E+01
1000.00	7.007E+01	7.007E+01	-1.689E+01	9.870E-20	8.696E+01
1200.00	6.969E+01	6.969E+01	-1.723E+01	3.461E-17	9.037E+01
1500.00	7.015E+01	7.015E+01	-1.692E+01	1.205E-14	9.552E+01
2000.00	7.559E+01	7.559E+01	-1.388E+01	5.072E-12	1.034E+02

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 2.3933E+09 n = .23844 Ea = 7.2170E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.768E+09	3.896E+00	2.400E-43	2.452E-43
400.00	5.376E+09	4.173E+00	3.634E-30	3.667E-30
500.00	5.917E+09	4.401E+00	3.067E-22	2.982E-22
600.00	5.761E+09	4.597E+00	5.927E-17	5.641E-17
800.00	4.857E+09	4.923E+00	2.342E-10	2.258E-10
1000.00	4.246E+09	5.192E+00	2.057E-06	2.091E-06
1200.00	4.280E+09	5.423E+00	8.654E-04	9.293E-04
1500.00	6.273E+09	5.719E+00	3.767E-01	4.171E-01
2000.00	3.857E+10	6.125E+00	2.114E+02	1.901E+02

THERMODYNAMIC ANALYSIS for REACTION

Rx **N(N2H3)(CH3)2 = T_N(N2H3)(CH3)2**

Hf {Kcal/mol} 54.650 121.440

S {cal/mol K} 92.230 77.840

Fit Af/Ar : A = 5.971E-02 n = -.82 alpha =-2.303E-03 avg error 33.46 %

Fit Af/Ar w/ddU: A = 1.933E+01 n = -1.86 alpha =-4.231E-03 avg error 75.76 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	6.680E+01	6.680E+01	-1.436E+01	1.564E-52	7.111E+01
400.00	6.716E+01	6.716E+01	-1.332E+01	2.471E-40	7.248E+01
500.00	6.737E+01	6.737E+01	-1.284E+01	5.543E-33	7.379E+01
600.00	6.748E+01	6.748E+01	-1.264E+01	4.531E-28	7.506E+01
800.00	6.751E+01	6.751E+01	-1.258E+01	6.366E-22	7.758E+01
1000.00	6.753E+01	6.753E+01	-1.257E+01	3.112E-18	8.010E+01
1200.00	6.777E+01	6.777E+01	-1.236E+01	9.039E-16	8.260E+01
1500.00	6.897E+01	6.897E+01	-1.148E+01	2.762E-13	8.619E+01
2000.00	7.491E+01	7.491E+01	-8.139E+00	1.084E-10	9.118E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 8.1148E+04 n = 1.80800 Ea = 6.6422E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	4.537E+09	3.010E+04	9.778E-40	9.899E-40
400.00	1.020E+10	5.064E+04	2.059E-27	2.087E-27
500.00	1.625E+10	7.581E+04	5.775E-20	5.671E-20
600.00	2.155E+10	1.054E+05	5.664E-15	5.445E-15
800.00	2.960E+10	1.773E+05	1.061E-08	1.026E-08
1000.00	3.736E+10	2.655E+05	6.484E-05	6.540E-05
1200.00	4.983E+10	3.691E+05	2.260E-02	2.390E-02
1500.00	9.693E+10	5.525E+05	8.634E+00	9.401E+00
2000.00	6.933E+11	9.295E+05	4.518E+03	4.156E+03

THERMODYNAMIC ANALYSIS for REACTION

Rx **CH(N2H3)(CH3)2 = T_CH(N2H3)(CH3)2**
Hf {Kcal/mol} 32.000 82.680
S {cal/mol K} 90.760 80.280

Fit Af/Ar : A = 4.591E-07 n = 1.86 alpha = 2.905E-03 avg error 29.87 %
Fit Af/Ar w/ddU: A = 3.900E-08 n = 2.45 alpha = 4.520E-03 avg error 73.64 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	5.069E+01	5.069E+01	-1.044E+01	6.110E-40	5.382E+01
400.00	5.118E+01	5.118E+01	-9.006E+00	1.157E-30	5.479E+01
500.00	5.145E+01	5.145E+01	-8.404E+00	4.702E-25	5.565E+01
600.00	5.152E+01	5.152E+01	-8.270E+00	2.656E-21	5.648E+01
800.00	5.120E+01	5.120E+01	-8.714E+00	1.280E-16	5.817E+01
1000.00	5.045E+01	5.045E+01	-9.540E+00	7.715E-14	5.999E+01
1200.00	4.949E+01	4.949E+01	-1.041E+01	5.119E-12	6.199E+01
1500.00	4.820E+01	4.820E+01	-1.138E+01	3.083E-10	6.527E+01
2000.00	4.741E+01	4.741E+01	-1.187E+01	1.681E-08	7.114E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 1.2241E+11 n = .14997 Ea = 5.2055E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.264E+10	2.352E+00	3.819E-27	3.418E-27
400.00	8.964E+10	2.456E+00	9.642E-18	1.081E-17
500.00	1.517E+11	2.540E+00	4.899E-12	5.461E-12
600.00	1.947E+11	2.610E+00	3.321E-08	3.481E-08
800.00	2.076E+11	2.725E+00	2.133E-03	2.000E-03
1000.00	1.713E+11	2.818E+00	1.607E+00	1.446E+00
1200.00	1.325E+11	2.896E+00	1.280E+02	1.170E+02
1500.00	1.018E+11	2.994E+00	9.636E+03	9.529E+03
2000.00	1.062E+11	3.126E+00	7.006E+05	7.835E+05

THERMODYNAMIC ANALYSIS for REACTION

Rx **S(N2H3)(CNH4) = T_S(N2H3)(CNH4)**
Hf {Kcal/mol} 54.540 96.480
S {cal/mol K} 99.040 83.950

Fit Af/Ar : A = 1.082E-01 n = -1.02 alpha =-1.786E-03 avg error 7.67 %
Fit Af/Ar w/ddU: A = 7.026E+00 n = -1.81 alpha =-3.169E-03 avg error 13.64 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	4.194E+01	4.194E+01	-1.509E+01	1.400E-34	4.647E+01
400.00	4.196E+01	4.196E+01	-1.502E+01	6.127E-27	4.797E+01
500.00	4.196E+01	4.196E+01	-1.502E+01	2.362E-22	4.947E+01
600.00	4.196E+01	4.196E+01	-1.503E+01	2.695E-19	5.098E+01
800.00	4.197E+01	4.197E+01	-1.501E+01	1.786E-15	5.398E+01
1000.00	4.208E+01	4.208E+01	-1.490E+01	3.527E-13	5.697E+01
1200.00	4.235E+01	4.235E+01	-1.465E+01	1.214E-11	5.993E+01
1500.00	4.319E+01	4.319E+01	-1.404E+01	4.360E-10	6.424E+01
2000.00	4.592E+01	4.592E+01	-1.248E+01	1.789E-08	7.089E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 5.5770E+05 n = 1.40461 Ea = 4.1547E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	3.149E+09	3.016E+03	8.749E-22	9.042E-22
400.00	4.336E+09	4.517E+03	5.106E-14	5.002E-14
500.00	5.438E+09	6.180E+03	2.461E-09	2.375E-09
600.00	6.497E+09	7.984E+03	3.369E-06	3.265E-06
800.00	8.725E+09	1.196E+04	2.977E-02	2.972E-02
1000.00	1.156E+10	1.636E+04	7.348E+00	7.575E+00
1200.00	1.571E+10	2.114E+04	3.036E+02	3.192E+02
1500.00	2.673E+10	2.892E+04	1.363E+04	1.425E+04
2000.00	7.781E+10	4.332E+04	7.455E+05	6.960E+05

THERMODYNAMIC ANALYSIS for REACTION

Rx **S(N2H3)2 = T_S(N2H3)2**
Hf {Kcal/mol} 83.190 124.980
S {cal/mol K} 96.620 82.730

Fit Af/Ar : A = 1.326E-01 n = -1.04 alpha =-2.586E-03 avg error 15.31 %
Fit Af/Ar w/ddU: A = 2.533E-01 n = -1.27 alpha =-3.906E-03 avg error 34.58 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	4.178E+01	4.178E+01	-1.391E+01	3.293E-34	4.596E+01
400.00	4.158E+01	4.158E+01	-1.450E+01	1.286E-26	4.738E+01
500.00	4.152E+01	4.152E+01	-1.465E+01	4.460E-22	4.884E+01
600.00	4.158E+01	4.158E+01	-1.454E+01	4.739E-19	5.030E+01
800.00	4.202E+01	4.202E+01	-1.392E+01	3.003E-15	5.315E+01
1000.00	4.277E+01	4.277E+01	-1.309E+01	6.185E-13	5.586E+01
1200.00	4.372E+01	4.372E+01	-1.223E+01	2.318E-11	5.839E+01
1500.00	4.526E+01	4.526E+01	-1.108E+01	9.630E-10	6.188E+01
2000.00	4.732E+01	4.732E+01	-9.878E+00	4.675E-08	6.708E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 1.4245E+03 n = 2.27429 Ea = 4.0404E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	5.705E+09	4.302E+05	2.058E-21	2.243E-21
400.00	5.647E+09	8.276E+05	1.072E-13	9.865E-14
500.00	6.559E+09	1.375E+06	4.646E-09	4.266E-09
600.00	8.315E+09	2.081E+06	5.924E-06	5.672E-06
800.00	1.510E+10	4.004E+06	5.006E-02	5.217E-02
1000.00	2.871E+10	6.651E+06	1.289E+01	1.398E+01
1200.00	5.317E+10	1.007E+07	5.796E+02	6.273E+02
1500.00	1.184E+11	1.672E+07	3.010E+04	3.088E+04
2000.00	2.890E+11	3.217E+07	1.948E+06	1.761E+06

THERMODYNAMIC ANALYSIS for REACTION

Rx **CH(N2H3)(CH3)2 = T_CH(N2H3)(CH3)2**
Hf {Kcal/mol} 19.210 85.030
S {cal/mol K} 92.290 82.580

Fit Af/Ar : A = 2.369E-10 n = 3.13 alpha = 3.639E-03 avg error 42.30 %
Fit Af/Ar w/ddU: A = 2.623E-17 n = 6.06 alpha = 7.331E-03 avg error 90.29 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	6.582E+01	6.582E+01	-9.720E+00	8.393E-51	6.873E+01
400.00	6.575E+01	6.575E+01	-9.936E+00	8.003E-39	6.972E+01
500.00	6.583E+01	6.583E+01	-9.747E+00	1.234E-31	7.071E+01
600.00	6.603E+01	6.603E+01	-9.385E+00	7.836E-27	7.166E+01
800.00	6.660E+01	6.660E+01	-8.568E+00	8.518E-21	7.346E+01
1000.00	6.714E+01	6.714E+01	-7.966E+00	3.838E-17	7.511E+01
1200.00	6.736E+01	6.736E+01	-7.761E+00	1.084E-14	7.667E+01
1500.00	6.638E+01	6.638E+01	-8.458E+00	3.008E-12	7.907E+01
2000.00	5.994E+01	5.994E+01	-1.208E+01	6.447E-10	8.410E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 7.7914E+06 n = 1.44220 Ea = 6.5554E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	4.692E+10	3.737E+03	5.246E-38	5.061E-38
400.00	5.614E+10	5.658E+03	6.670E-26	6.674E-26
500.00	7.715E+10	7.806E+03	1.286E-18	1.343E-18
600.00	1.111E+11	1.015E+04	9.796E-14	1.043E-13
800.00	2.234E+11	1.538E+04	1.420E-07	1.474E-07
1000.00	3.782E+11	2.121E+04	7.997E-04	7.767E-04
1200.00	5.031E+11	2.759E+04	2.710E-01	2.469E-01
1500.00	4.428E+11	3.807E+04	9.403E+01	8.321E+01
2000.00	9.543E+10	5.764E+04	2.686E+04	3.079E+04

THERMODYNAMIC ANALYSIS for REACTION

Rx **C(N2H3)(CH3)3 = T_C(N2H3)(CH3)3**

Hf {Kcal/mol}	16.110	81.640
S {cal/mol K}	102.400	93.720

Fit Af/Ar : A = 6.734E+01 n = -1.57 alpha =-2.918E-03 avg error 37.41 %
Fit Af/Ar w/ddU: A = 5.991E+05 n = -3.23 alpha =-5.511E-03 avg error 83.15 %

T (K)	dH(Kcal/mol)	dU(Kcal/mol)	dS(cal/mol K)	Kc	dG(Kcal/mol)
300.00	6.554E+01	6.554E+01	-8.656E+00	2.293E-50	6.813E+01
400.00	6.583E+01	6.583E+01	-7.789E+00	2.111E-38	6.895E+01
500.00	6.597E+01	6.597E+01	-7.475E+00	3.368E-31	6.971E+01
600.00	6.599E+01	6.599E+01	-7.432E+00	2.163E-26	7.045E+01
800.00	6.586E+01	6.586E+01	-7.627E+00	2.191E-20	7.196E+01
1000.00	6.573E+01	6.573E+01	-7.767E+00	8.615E-17	7.350E+01
1200.00	6.591E+01	6.591E+01	-7.607E+00	2.146E-14	7.504E+01
1500.00	6.727E+01	6.727E+01	-6.621E+00	5.635E-12	7.720E+01
2000.00	7.362E+01	7.362E+01	-3.042E+00	1.947E-09	7.971E+01

The model fitted is for uni-molecular reaction.

The 3 parameters for the model equation of A(T) = Aprime * T^n * exp(-Ea/RT)
Aprime = 7.8438E+06 n = 1.54493 Ea = 6.5272E+04

Temp(K)	AF(T)	T_K^n	k_calc(T)	k_fit
300.00	8.018E+10	6.714E+03	1.433E-37	1.468E-37
400.00	1.654E+11	1.047E+04	1.759E-25	1.772E-25
500.00	2.422E+11	1.478E+04	3.508E-18	3.400E-18
600.00	2.969E+11	1.959E+04	2.705E-13	2.566E-13
800.00	3.588E+11	3.055E+04	3.652E-07	3.520E-07
1000.00	4.181E+11	4.313E+04	1.795E-03	1.832E-03
1200.00	5.436E+11	5.716E+04	5.365E-01	5.794E-01
1500.00	1.117E+12	8.070E+04	1.761E+02	1.952E+02
2000.00	9.014E+12	1.259E+05	8.115E+04	7.264E+04